METHODS OF SAMPLING AND TESTING
MT 532-16
DETERMINATION OF SULFATE CONTENT IN SOILS BY ION CHROMATOGRAPHY

1 Scope

1.1 This method describes the procedures used to determine water-soluble sulfate in soils through the use of the ion chromatograph (IC).

1.2 This method was developed as an alternative to the sulfate analysis in MT 232 and was validated June 2016.

1.3 This method may involve hazardous materials, operations, and equipment. This method does not purport to address all of the safety concerns associated with its use. It is the responsibility of the user of this procedure to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to use.

2 Referenced Documents

ASTM
C1580 Standard Test Method for Water-Soluble Sulfate in Soil
D1193 Standard Specification for Reagent Water

MT Materials Manual
MT 232 Soil Corrosion Test

Other
TX DOT, Tex-620-J, Determining Chloride and Sulfate Contents in Soil (http://ftp.dot.state.tx.us/pub/txdot-info/cst/TMS/600-J_series/archives/620-0805.pdf)
Validation of Sulfate Method on the Ion Chromatograph, MDT, June 2016.

3 Summary of Test Method

3.1 Soils are dissolved in water and analyzed on the ion chromatograph. This method is substantially based on ASTM C1580 and the Texas Department of Transportation Method Tex-620-J. The method of analysis can be used for both solid soil and water samples. The samples are dissolved or diluted in water, filtered and injected into the IC instrument. A calibration curve is prepared on the IC using a five anion standard. Sulfate results are obtained in ppm as determined by the IC.

4 Significance and Use

4.1 This procedure is used to determine sulfate content in soil samples for pipe corrosion evaluation and soil survey samples.

5 Apparatus

5.1 *Metrohm Basic Ion Chromatograph Plus 883* equipped with:

5.1.1 Autosampler

5.1.2 Metrosep A Supp 150/4.0 Column

5.1.3 Conductivity Detector

5.1.4 MagIC Net Software

6 Reagents and Materials

6.1 *Reagent Water* – Purified water that meets ASTM Type II specifications or better (ASTM D1193)

6.2 *Suppressor Regenerant Solution*, 0.1M Sulfuric Acid, H_2SO_4 (aqueous)

6.3 *Suppressor Rinse Solution*, 99.9% MeOH

6.4 *Eluent*, 3.2 M Sodium Carbonate, Na_2CO_3/1.0 M Sodium Bicarbonate, $NaHCO_3$ (aqueous); (stock eluent solution, A Supp 5 Eluent 100x, ordered from Metrohm and kept in-house).

6.5 *Standard Stock Solution*, Dionex Five Anion Standard, Sulfate concentration of 150 mg/L

6.6 *Glassware*: 250 mL beakers and large glass centrifuge tubes

6.7 *Class A pipettes*, for secondary dilution

6.8 *Plastic Syringes*, 30 mL non-sterile

6.9 *0.20 µm nylon filters*, non-sterile

7 Sampling

7.1 Samples are prepared in accordance with MT 232. A 3 gram (g) sample is required for analysis.

8 Calibration and Standardization

8.1 *IC Instrumentation Settings*

8.1.1 Flow rate on IC: 0.7 mL/min

8.1.2 Sample Loop: 20 µL

8.1.3 Run time: 20 minutes

8.2 *Calibration Curve Determination*

8.2.1 Prepare six standards based on the indicated concentrations and masses in Table 1 using the Dionex Five Anion Standard. The values for the sulfate calibration curve range from approximately 2.5 ppm and 50 ppm.

8.2.2 Weigh the standard into a plastic bottle. Record weights to the thousandth decimal place.

8.2.3 Dilute the standard to a target total mass of 50 (±0.001g) with reagent water. Record the final weight.

Table 1: Standard calibration solutions and masses of components

Concentration, ppm	Mass of 5 anion standard, g	Mass of solution, g
2.5	0.834	50.000
5	1.667	50.000
10	3.334	50.000
20	6.667	50.000
25	8.334	50.000
50	16.668	50.000

Note 1 - The masses in Table 1 above have been developed for the Dionex Five Anion Standard which has a sulfate concentration of 150 ppm, if another standard is used the weights in the table are not applicable

8.2.4 Inject the six prepared standards and utilize the instrumentation on the IC to develop a calibration curve.

9 Procedure

9.1 *Preparation of Controls*

For each sequence to be analyzed on the IC, prepare a Quality Control (QC) sample in the target range of approximately 20 ppm. Use a qualified soil standard with a known concentration of 1630 ppm (±43.7 ppm) to prepare the control. Determine percent recovery per Section 10.4 below. Analysis is considered acceptable with a percent recovery on the control sample of ±10%.

9.2 *Sample Preparation and Analysis*

9.2.1 Weigh 3 grams of sample from the remaining material used for the conductivity preparation in MT 232 into a 250 ml glass beaker. Record the weight to the thousandth decimal place (W_s).

9.2.2 Add 150 mL of reagent water and mix with a stir bar for an hour.

9.2.3 Pour approximately 20 mL of the liquid extract into a syringe with attached 0.20 µm nylon filter. Filter this extract directly into plastic ion chromatography test tube and cap.

9.2.4 Analyze the sample and the QC sample simultaneously on the IC to determine the sulfate concentrations.

Note 2 – A secondary dilution may be necessary if concentration falls outside of the range determined by the calibration curve.

10 Calculation or Interpretation of Results

10.1 *Dilution Factor*

$$DF = \frac{Vf}{Vi}$$

Where:
DF = Dilution factor
Vf = Final volume (diluent and aliquot)
Vi = initial volume

10.1.1 Dilution Factor for Secondary Dilution

$$DF = \frac{Vd}{Vp}$$

Where:
DF = Dilution factor
Vd = Volume of the flask used for the dilution, mL
Vp = Volume of the pipette used to make the dilution, mL

10.2 *Concentration of sulfate ion in the original soil sample*

$$C_{SO4} = (C_{IC}*DF)/W_s$$

Where:
C_{SO4} = Concentration of the sulfate in the original soil sample, ppm
C_{IC} = concentration of sulfate ion in the sample run through the IC, ppm
DF = Dilution factor
W_s = Weight of the sample, g

10.2.1 Example: C_{IC} = 2.948 mg/L (*or ppm)*
DF = 150
W_s= *3.0041 g*

C_{SO4}= *(*2.948*150)/3.0041 = 147.2 ppm

10.3 *Percent Sulfate in Soil*

$$\% SO_4 = C_{SO4}/10{,}000$$

10.4 *Percent Recovery Quality Control Sample*

$$\% \text{ Recovery} = [C_{IC(QC)}*DF/W_{QC}/10{,}000/C_{QC}]*100\%$$

Where:
$C_{IC(QC)}$ = Concentration of the soil standard sample as determined by the IC, ppm
C_{QC} = Known value of the soil standard (soil standard typically is 1630 ppm SO_4), ppm
DF = Dilution factor
W_{QC} = Weight of the quality control sample, g

10.4.1 Example: $C_{IC(QC)}$ = 31.96 ppm
DF = 50
W_{QC}= *1.004 g*
C_{QC} = *1630 ppm*

% Recovery = [31.96*50/1.004/1630]*100 = 98.07%

11 Report

The concentration of the sulfate will be recorded in the soil corrosion spreadsheets and the Sitemanager data base as percent sulfate.